


PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B01J 31/02	A1	(11) International Publication Number: WO 00/16902 (43) International Publication Date: 30 March 2000 (30.03.00)
(21) International Application Number: PCT/GB99/03150 (22) International Filing Date: 22 September 1999 (22.09.99) (30) Priority Data: 9820698.0 24 September 1998 (24.09.98) GB (71) Applicants (for all designated States except US): BP CHEMICALS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB). AKZO NOBEL NV [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). ELEMENTIS UK LIMITED [GB/GB]; One Great Tower Street, London EC3R 5AH (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): KEIM, Willi [DE/DE]; Brüsseler Ring 99, D-52074 Aachen (DE). KORTH, Wolfgang [DE/DE]; Jakobstrasse 75-77, D-52064 Aachen (DE). WASSERSCHIED, Peter [DE/DE]; Greven Broicher Strasse 2, D-50829 Köln (DE). (74) Agent: COLLINS, Frances, Mary; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: IONIC LIQUIDS (57) Abstract An ionic liquid which is substantially free of Lewis acidity wherein said ionic liquid is obtainable by reacting (a) an organo-nitrogen compound or an organo-phosphorus compound which is substantially free of Lewis acidity with (b) a Brønsted acid, in a mole ratio of (a) to (b) of less than or equal to 1 with the proviso that where the Brønsted acid gives up a single proton the mole ratio of (a) to (b) is less than 1. The ionic liquids are useful as acid catalysts or as solvents for acid catalysts, for example, in esterification reactions or in the alkylation of aromatics. 		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

IONIC LIQUIDS

This invention relates to novel ionic liquids and use thereof as a catalyst or as a solvent for acid catalysts in chemical reactions.

Ionic liquids are primarily a mixture of salts which are liquid at or below ambient temperatures. Such mixtures have conventionally included (alkyl) aluminium halides in combination with one or more imidazolium halides or pyridinium halides which in turn may be substituted in their respective rings by one or more hydrocarbyl groups. Such ionic liquids usually consist of a mixture in which the mole ratio of the (alkyl)aluminium halide to the imidazolium or pyridinium halide is usually > 1.0 and they invariably have Lewis acidity. The presence of an (alkyl) aluminium halide - which in itself is a Lewis acid - in ionic liquids of this type enables the acidity of any conventional acids - whether Lewis or Brønsted acids - combined therewith or dissolved in such ionic liquids to display enhanced acidity which is to be expected due to the reinforcing effect of the two acidic components. It is however, more difficult to envisage an ionic liquid displaying acidity when the ionic liquid itself is substantially free of Lewis acidity, which Lewis acidity is usually conferred upon such liquids by the presence of e.g. organo-aluminium compounds therein, and when it is combined with an acid such as e.g. a Brønsted acid.

EP-A-0748653 relates to ionic salts of the general formula Q^+A^- where Q^+ represents a quaternary ammonium and/or phosphonium salt and A^- represents any known anion which can form a liquid salt at low temperatures. An example of a suitable salt disclosed is 3-butyl-1-methylimidazolium hexafluorophosphate. The ionic salts are used as solvents or can be used in combination with transition metal complexes to catalyst hydrogenation reactions. Such ionic liquid salts are neutral

It has now been found that by using ionic liquids having Brønsted acidity, which

are substantially free of Lewis acidity, these can be used as acid catalysts as such or as solvents for conventional acid catalysts.

Accordingly, the present invention provides an ionic liquid which is substantially free of Lewis acidity wherein said ionic liquid is obtainable by reacting (a) an organo-
 5 nitrogen compound or an organo-phosphorus compound which is substantially free of Lewis acidity with (b) a Brønsted acid, in a mole ratio of (a) to (b) of less than or equal to 1 with the proviso that where the Brønsted acid gives up a single proton the mole ratio of (a) to (b) is less than 1

The definitions of Lewis and Brønsted acids are well known. For instance such a
 10 definition can be found in 'Organic Chemistry' by Morrison and Boyd, Eds. Allyn & Bacon, New York Univ. pp. 32-34, 1973. Thus, by "Lewis" acid as used herein and throughout the specification is meant a compound or an acid that is an electron pair acceptor which thereby enables said compound or acid to form a covalent bond. Thus, hydroxide ions, ammonia and water are bases because they contain electron pairs
 15 available for sharing. In boron trifluoride, boron has only six electrons in its outer shell and hence tends to accept another pair to complete its octet. Boron trifluoride is an acid and combines with such bases as ammonia or ethyl ether. Aluminium trichloride is an acid and, stannic chloride, even though the latter has a complete octet, is an acid because it is capable of accepting additional pairs of electrons to form e.g. divalent tin
 20 hexachloride (SnCl_6^{2-}).

By 'Brønsted acid' is meant here and throughout the specification a compound or an acid that gives up a proton. Thus, when sulphuric acid dissolves in water, the acid gives up a proton to the base water to form new, relatively weaker acids H_3O^+
 25 (hydronium ion) and HSO_4^- (hydrogen sulphate ion). According to this definition, the strength of an acid depends upon its tendency to give up a proton. Sulphuric acid and hydrogen chloride are strong acids since they tend to give up a proton very readily.

By 'Brønsted acid that gives up a single proton' is meant here and throughout the specification a Brønsted acid which contains only one hydrogen e.g. HNO_3 or HPF_6 .

30 Examples of Brønsted acids that may be used to prepare the ionic liquids of the present invention include those capable of generating the following anions in the ionic liquid, BF_4^- , PF_6^- , RCOO^- , CF_3COO^- , $\text{HO}(\text{O})\text{C}-\text{C}(\text{O})\text{O}^-$, $\text{HO}(\text{O})\text{C}.\text{CH}_2-\text{C}(\text{OH})(\text{COOH})-\text{CH}_2.\text{C}(\text{O})\text{O}^-$, RNO_3^- , CF_3SO_3^- , H_2PO_4^- , RPO_3H^- , RSO_3^- , ROPO_3^- , ROSO_3^- and HSO_4^-

wherein R represents a C1-C30 hydrocarbyl group which may be straight or branched chain, saturated or unsaturated. Preferably, the hydrocarbyl group is an alkyl, cycloalkyl, aryl, alkaryl or aralkyl group. The hydrocarbyl group may be optionally further substituted with a group containing nitrogen, oxygen, sulphur, silicon or halogen atoms.

5 Specifically, the respective Brønsted acids from which these anions may be derivable are HBF_4 , HPF_6 , acetic acid, trifluoroacetic acid, oxalic acid, citric acid, HNO_3 , trifluorosulphonic acid, H_3PO_4 , a partial ester of phosphoric acid, a partial ester of sulphuric acid and H_2SO_4 . Such Brønsted acids may be used singly or as a mixture of one or more such acids thereby generating one anion corresponding to each Brønsted

10 acid used. Preferably, the Brønsted acid used is capable of giving up at least 2 protons, such as H_2SO_4 or H_3PO_4 .

The organo-nitrogen compounds used in making the ionic liquids may be substituted or unsubstituted aliphatic, alicyclic, aromatic or heterocyclic amines. The amines may be primary, secondary or tertiary amines. Where such amines are non-cyclic

15 compounds substituted by a hydrocarbyl group such substituents may be derived from saturated or unsaturated, aliphatic, alicyclic, cycloaliphatic or aromatic hydrocarbons. The amines are suitably tertiary amines and may be selected from trialkyl amines, triaryl amines, alkyl diaryl amines, aryl dialkyl amines or any combinations thereof. In particular, aliphatic amines such as e.g. triethyl amines, trimethyl phenylamines and

20 heterocyclic amines such as dialkyl imidazoles, pyrazoles and pyridines may be used with particular advantage. In the dialkyl imidazoles and the pyridines, the alkyl groups may be the same or different e.g. 1-methyl-3-ethylimidazole, 1-methyl-3-butylimidazole, 1-ethyl-3-butylimidazole, 1-hexyl-3-methylimidazole, dimethylimidazoles and diethylimidazoles, and the corresponding dialkyl derivatives of pyrazole and pyridine. In respect of the

25 imidazoles and their salts, it should be noted that the 1- and 3- positions are interchangeable due to the symmetrical nature of the imidazole ring. The organo-nitrogen compound may have cations represented by the generic formula $[\text{NR}^1\text{R}^2\text{R}^3\text{R}^4]^+$ or $[\text{R}^1\text{R}^2\text{N}=\text{CR}^3-\text{R}^5-\text{R}^3\text{C}=\text{N}^+\text{R}^2\text{R}^1]$ wherein R^1-R^4 can be the same or different and is selected from H or a hydrocarbyl group with the proviso that at least one of R^1-R^4 is a

30 hydrocarbyl group and R^5 is an alkylene group (e.g. CH_2 , CH_2CH_2 etc type group) or a phenylene group (e.g. C_6H_4 type group). The hydrocarbyl group is preferably a C1-C30 hydrocarbyl group which may be straight or branched chain, saturated or unsaturated. Preferably, the hydrocarbyl group is an alkyl, cycloalkyl, aryl, alkaryl or aralkyl group.

In the preparation of the ionic liquid of the present invention, the above mentioned amines may be used as such. Alternatively, a salt of the amine may be used e.g. a chloride. The preparation of such amine salts is well known in the art.

The organo phosphorus compound used in making the ionic liquids of the present invention may contain cations of the formula $[PR^1R^2R^3R^4]^+$ or $[R^1R^2P=CR^3-R^5-R^3C=P^+R^2R^1]$ wherein R^1-R^5 have the same significance as described in the context of $[NR^1R^2R^3R^4]^+$ and $[R^1R^2N=CR^3-R^5-R^3C=N^+R^2R^1]$ above. Ionic liquids generated by reacting such an organo-phosphorus compound and a Brønsted acid will contain such cations. Examples of such ionic liquids include tetrabutylphosphonium tetrafluoroborate.

The ionic liquids of the present invention can be prepared by reacting one or more of the (a) organo-nitrogen or organo-phosphorus compounds with (b) one or more Brønsted acids in a mole ratio of (a) to (b) of less than or equal to 1 with the proviso that where the Brønsted acid gives up a single proton the mole ratio of (a) to (b) is less than 1. Suitably the mole ratio (a) to (b) is in the range from 0.00001 to 1, preferably in the range 0.001-0.96 and more preferably in the range from 0.01 to 0.05. Where the Brønsted acid gives up a single proton such as HNO_3 , ionic liquids according to the present invention may be suitably prepared by (i) reacting one or more of the organo-nitrogen or organo-phosphorus compounds with the Brønsted acid in a mole ratio of the organo-nitrogen or organo-phosphorus compounds to the Brønsted acid of equal to 1 to form a neutral ionic salt and (ii) adding further Brønsted acid (such that the mole ratio of (a) to (b) is less than 1) to the neutral ionic salt to form an ionic liquid according to the present invention.

Due to the varied nature of the reactants the temperature at which (a) and (b) react may vary over a moderate range of temperature conditions such as e.g. from ambient to about $150^\circ C$. The duration of the reaction may vary over a moderately wide range such as from about a few minutes to about a few days, for example, a week. The resultant products may then be purified to remove any unwanted ions or salts and any adventitious products such as water. The ionic liquids, as the name implies, are generally liquids. However, if any of them are solids at room temperature, they should be transformable into liquids by applying a small amount of heat, i.e. they are liquids at or below $80^\circ C$.

More specifically and, in particular 1-butyl-3-methyl imidazolium hydrogen

5 sulphate can be prepared by carefully adding concentrated aqueous sulphuric acid (0.13 mole) to a cold (e.g. 0°C) solution of 1-butyl-3-methylimidazolium chloride, (0.13 mole) in a solvent such as dry methylene chloride. The admixture is then refluxed for a sufficient duration (for example, two days) to enable the reaction to be completed and any hydrogen chloride by-product to be removed therefrom. The solution is then cooled down to room temperature and finally the methylene chloride is removed under vacuum. The water present in the reaction mixture from the aqueous sulphuric acid used may be then removed by azeotropic distillation with, for example, benzene, to leave behind a clear pale yellow ionic liquid. The product, when dried as described above, was found to be highly hygroscopic and was therefore stored under an inert atmosphere and/or solvent. The product was characterised by NMR spectroscopy.

Similarly, ionic liquids having H_2PO_4^- anions derived from e.g. phosphoric acid or a salt thereof such as potassium dihydrogenphosphate may also be prepared as substantially described above.

15 Alternatively, where one or more of the reactants is a solid at ambient temperature, the reactants may be heated together to form a melt. Subsequent dissolution of the melt in a suitable solvent will yield the ionic liquid together with other reaction by-products which can be subsequently separated.

Any water which may be adventitiously introduced into such an ionic liquid from the source of anions used to prepare said ionic liquids may either be left in (or retained) in the ionic liquid - if such water is not likely to adversely affect any subsequent reaction in which the ionic liquid is used - or, alternatively, it may be removed from the ionic liquid e.g. by evaporation.

Specific examples of ionic liquids according to the invention include 1-butyl-3-methyl imidazolium hydrogen sulphate, triethylammonium hydrogen sulphate, trioctyl ammonium hydrogen sulphate, 1-ethyl-3-methyl imidazolium dihydrogen phosphate and 1-hexyl-3-methyl imidazolium dihydrogen phosphate. Such ionic liquids have been characterised by NMR spectroscopy as shown in the Examples below. 1-butyl-3-methyl imidazolium hydrogen sulphate, triethylammonium hydrogen sulphate, trioctyl ammonium hydrogen sulphate may be derived by reacting 1-butyl-3-methylimidazolium chloride, triethylamine, trioctylamine, respectively with a suitable source of HSO_4^- anions such as e.g. sulphuric acid in a mole ratio of nitrogen compound to sulphuric acid of e.g. less than 1 or equal to 1. 1-ethyl-3-methyl imidazolium dihydrogen phosphate and 1-

hexyl-3-methyl imidazolium dihydrogen phosphate may be derived by reacting 1-ethyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride, respectively, with a suitable source of H_2PO_4^- anions such as e.g. ortho-phosphoric acid or potassium dihydrogenphosphate in a mole ratio of nitrogen compound to Brønsted acid of less than or equal to 1.

The ionic liquids of the present invention exhibit may exhibit weak Brønsted acidity due for instance to a residual 'proton' such as e.g. in the HSO_4^- anion.

A feature of the ionic liquids of the present invention is that they may be used as catalysts themselves (where the ionic liquid has weak Brønsted acidity) or as a solvent for conventional acidic catalysts used in any acid-catalysable chemical reaction.

In the case where the Brønsted acid is capable of giving up at least 2 protons e.g. H_2SO_4 or H_3PO_4 and the mole ratio of the organo-nitrogen or organo-phosphorus compound to the Brønsted acid is equal to 1, the resulting ionic liquid is weakly acidic. For some acid catalysed reactions this level of acidity may be insufficient to impart good reaction performance. In such a case, addition of excess Brønsted acid to the ionic liquid increases the acidity of the ionic liquid thereby improving the reaction performance.

According to yet another embodiment of the present invention there is provided a chemical reaction catalysed by an acid catalyst, characterised in that the acid catalyst is an ionic liquid which is substantially free of Lewis acidity and wherein said ionic liquid is obtainable by reacting (a) an organo-nitrogen compound or an organo-phosphorus compound which is substantially free of Lewis acidity with (b) a Brønsted acid which is capable of giving up at least two protons, in a mole ratio of (a) to (b) of equal to 1.

According to yet a further embodiment of the present invention there is provided a chemical reaction catalysed by an acid catalyst, characterised in that the acid catalyst is dissolved in an ionic liquid which is substantially free of Lewis acidity and wherein said ionic liquid is obtainable by reacting (a) an organo-nitrogen compound or an organo-phosphorus compound which is substantially free of Lewis acidity with (b) a Brønsted acid, in a mole ratio of (a) to (b) of less than or equal to 1 with the proviso that where the Brønsted acid gives up a single proton the mole ratio of (a) to (b) is less than 1.

Examples of chemical reactions catalysed by acid catalysts in which the ionic liquids of the present invention may be used as an acid catalyst per se or as a solvent for an acid catalyst include esterification, polymerisation of olefins, oligomerisation, alkylation of aromatics, alkylation of isobutane with olefins and the production e.g. of

caprolactam.

A further feature of the ionic liquids of the present invention or any acid catalysts dissolved therein is that the ionic liquids or solution of acids therein are stable liquids under conditions in the range of -100°C to about 300°C , typically from -100°C to about $+100^{\circ}\text{C}$ and at pressures ranging from 1-200 bar.

The advantage of using the ionic liquids of the present invention in acid catalysed reaction systems is that the solubility and/or intrinsic acidity of the Brønsted acid can be modified by the choice of the salt or the base used as a source of cations in the ionic liquid. Such modification of the Brønsted acid improves acid catalysed reaction performance characteristics e.g. reactivity and/or selectivity of the catalyst. In addition, use of such ionic liquids facilitates the separation of the reactants and products from the catalyst due to the high solvating effect of the ionic liquid for the acid catalyst. This feature also minimises the loss of the acid catalyst which is normally associated with separation process involving conventional distillation or flashing off processes.

The present invention is further illustrated with reference to the following Examples:

1. Synthesis of triethylammonium hydrogen sulphate

Triethylamine (10.08 mg, 0.1 mol) was reacted with sulphuric acid (5.5 ml concentrated sulphuric acid, 0.1 mol) in water (100 ml) for 15 minutes with stirring, the acid being added to a cold stirred amine. The water was then removed by heating under vacuum (10 mbar) at 80°C until water was shown to be absent by infra-red analysis. The resultant product (18.3 g) was a white, crystalline solid (yield 92%). The product upon analysis by NMR had the following characteristics:

$^1\text{H-NMR}$ (CD_3CN): $\delta=8.65$ (br, 1H, HSO_4); 8.36 (s, 1H, HN); 3.16 (m, 6H,

$\text{N}[\text{CH}_2\text{CH}_3]_3$); 1.28 (m, $\text{N}[\text{CH}_2\text{CH}_3]_3$)

$^{13}\text{C-NMR}$ (CD_3CN): $\delta=46.15$ ($\text{N}[\text{CH}_2\text{CH}_3]_3$); 7.77 ($\text{N}[\text{CH}_2\text{CH}_3]_3$).

C, H, N Analysis:

Element	Calculated (%)	Experimental (%)
C	36.165	36.13
H	8.598	8.35
N	7.029	6.87

The above data confirm the structure of the compound to be that of triethylammonium hydrogen sulphate ($\text{HNEt}_3^+\text{HSO}_4^-$).

2. Synthesis of 1-butyl-3-methyl imidazolium hydrogen sulphate:

In a flask equipped with a dropping funnel, a condenser and a magnetic stirrer 1-butyl-3-methylimidazolium chloride salt (22.12 g, 0.13 mol) was dissolved in dry methylene chloride (100 ml). The solution was cooled to 0°C with an ice bath. To this solution (13.06 g) was carefully added an aqueous solution of concentrated sulphuric acid (97.14 %, 0.13 mol). To obtain a hydrogen sulphate ionic liquid, the sulphuric acid and the organic salt were used in the same molecular ratios.

After the addition of the solution was completed, the mixture was heated under reflux for two days. From time to time any HCl by-product formed in the process which was distilling out of the condenser was monitored. When the formed HCl had been completely removed the solution was cooled to room temperature and the methylene chloride was removed carefully under vacuum.

To remove any water (generated from the aqueous sulphuric acid used) benzene (10 ml) was added to the viscous residue and the biphasic mixture was heated to 50°C to give a nearly homogeneous solution for several hours and the benzene/water azeotrope was then removed.

The cation⁺/HSO₄⁻ salt remained as a high viscous, clear pale yellow ionic liquid.

The product appeared to be very hygroscopic and hence was stored in an atmosphere inert under the conditions or in an inert solvent (e.g. hexane). The ionic liquid was characterised by nmr-spectroscopy.

NMR-Data:

¹H-NMR (CD₃CN): d= 11.02 (s, 1H, H_i); 8.99 (s, 1H, H_a); 7.50 (m, 2H, H_c H_d); 4.16 (t, 2H, H_e); 3.85 (s, 3H, H_b); 1.75 (m, 2H, H_f); 1.25 (m, 2H, H_g); 0.83 (t, 3H, H_h)

¹³C-NMR (CD₃CN): d = 137.759 (C_a); 124.59 (C_c); 123.207 (C_d); 49.963 (C_e); 36.729 (C_b); 32.616 (C_f); 19.884 (C_g); 13.765 (C_h)

3. Synthesis of trioctyl ammonium hydrogen sulphate

In a flask equipped with a dropping funnel, a condenser and a magnetic stirrer 161.8 g (0.46 mol) trioctylamine was dissolved in 200 ml of ether. The solution was stirred vigorously and 46.05 g (0.46 mol H₂SO₄) of an 18 molar concentrated sulphuric acid was carefully dropped into the solution. To obtain a hydrogen sulphate ionic liquid, the sulphuric acid and the amine were used in equimolar ratios. During the reaction the

solution became warmer.

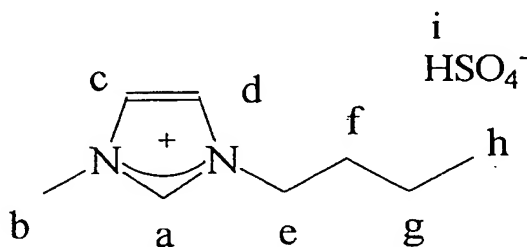
After completion of the addition, the resultant solution was stirred for 15 min. The solvent was removed carefully under vacuum room temperature. The

$[\text{HN}(\text{Octyl})_3]^+[\text{HSO}_4]^-$ salt remained as a white waxy crystalline solid. The product

appeared not to be very hygroscopic. The ionic liquid was characterised by nmr-spectroscopy. The yield of the product was 197 g (95 % of theory).

NMR-Data:

$^1\text{H-NMR}$ (CD_3CN): δ = 8.61 (br, 1H, HSO_4); 3.82 (s, 1H, HN); 3.03 (m, 6H, $\text{N}[\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3]_3$); 1.7 (tr, 6H, $\text{N}[\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3]_3$); 1.34 (m, 30H, $\text{N}[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]_3$); 0.92 (m, 9H, $\text{N}[\text{CH}_2\text{CH}_3]_3$)



4. Synthesis of 1-ethyl-3-methylimidazolium dihydrogen phosphate

1-ethyl-3-methylimidazolium chloride (33.8 g, 0.23mol) was dissolved in chloroform (150 cm³) in a round-bottomed flask equipped with a magnetic stir bar. The solution was cooled to 0°C. *o*-phosphoric acid (90%, 14.8 cm³) was added drop-wise. After the addition was completed, the mixture was heated under reflux for about 5 hours, and then stirred at room-temperature for 48 hours; 2 phases formed. The lower phase was dried over magnesium sulphate, and the solvent removed under reduced pressure.

The ionic liquid formed was hygroscopic and a solid at room-temperature.

The ionic liquid was characterised by nmr-spectroscopy.

$^1\text{H-NMR}$ (D_2O , 300MHz): δ = 8.46(s, 1H, H(C-2)); 7.22 (d, 2H, H(C-4, C-5)); 4.0 (q, 2H, N-CH₂-CH₃); 3.59 (s, 3H, N-CH₃); 1.26 (t, 3H, N-CH₂-CH₃).

$^{13}\text{C-NMR}$ (D_2O , 300MHz): δ = 135.7 (C-2); 123.68, 122.08 (C-4, C-5); 45.0 (N-CH₂-

CH₃); 35.89 (N-CH₃); 14.74 (N-CH₂-CH₃).

³¹P (D₂O, 300MHz): A single peak appears at 2.0ppm. A sealed melting-point tube containing 90% H₃PO₄ was inserted as internal standard. Two clearly separated peaks appear, indicating the two different phosphorus species H₂PO₄⁻ and H₃PO₄.

5 **5. Synthesis of 1-ethyl-3-methylimidazolium dihydrogen phosphate**

1-ethyl-3-methylimidazolium chloride (35.4g, 0.24mol) was melted in a round-bottomed flask equipped with a magnetic stir bar by means of an oil-bath. KH₂PO₄ (25.6g, 0.24 mol) was added and the melt stirred for 24 hrs. After cooling to room-temperature, the resulting solid was dissolved in methanol, and the insoluble white powder (KCl) was filtered off. The methanol was removed under reduced pressure. The resulting ionic liquid was dissolved in the minimum amount of chloroform, and placed in a freezer overnight; residual KCl precipitated and was removed by filtration. The solvent was removed under reduced pressure.

The ionic liquid formed was hygroscopic and solid at room-temperature.

15 The ionic liquid was characterised by nmr-spectroscopy.

¹H-NMR (D₂O, 300MHz): δ = 8.60(s, 1H, H(C-2)); 7.18 (d, 2H, H(C-4, C-5)); 4.1 (q, 2H, N-CH₂-CH₃); 3.75 (s, 3H, N-CH₃); 1.51 (t, 3H, N-CH₂-CH₃).

¹³C-NMR (D₂O, 300MHz): δ = 135.5 (C-2); 123.4, 121.1 (C-4, C-5); 44.7 (N-CH₂-CH₃); 35.5 (N-CH₃); 14.4 (N-CH₂-CH₃).

20 ³¹P (D₂O, 300MHz): A single peak appears at 2.0ppm. A sealed melting-point tube containing 90% H₃PO₄ was inserted as internal standard. Two clearly separated peaks appear, indicating two different phosphorus species.

6 **6. Synthesis of 1-hexyl-3-methylimidazolium dihydrogen phosphate**

1-hexyl-3-methylimidazolium chloride (95.6g, 0.47mol) was dissolved in acetone (250 cm³) in a round-bottomed flask equipped with a magnetic stir bar. KH₂PO₄ (65.5g, 0.48mol) was added to this solution. The mixture was stirred for 2 days at room-temperature. The white precipitate (KCl) was removed by filtration. Acetone was removed on the rotary evaporator and the resulting ionic liquid was dissolved in a minimum amount of chloroform; This solution was placed in a freezer overnight.

30 Residual KCl precipitated and was removed by filtration. The solvent was removed under reduced pressure.

The ionic liquid formed was a yellow, hygroscopic and highly viscous liquid.

The ionic liquid was characterised by nmr-spectroscopy.

¹H-NMR (D₂O, 300MHz): δ = 8.8(s, 1H, H(C-2)); 7.5 (d, 2H, H(C-4, C-5)); 4.2 (t, 2H, N-CH₂-(CH₂)₄-CH₃); 3.9 (s, 3H, N-CH₃); 1.9 (t, 2H, N-CH₂-CH₂-(CH₂)₃-CH₃); 1.3 (m, 6H, N-CH₂-CH₂-(CH₂)₃-CH₃); 0.8 (t, 3H, N-(CH₂)₅-CH₃).

¹³C-NMR (D₂O, 300MHz): δ = 136.3 (C-2); 124.0, 122.8 (C-4, C-5); 50.0 (N-CH₂-(CH₂)₄-CH₃); 36.2 (N-CH₃); 30.8; 29.7; 25.5; 22.3 (N-CH₂-(CH₂)₄-CH₃); 13.8 (N-(CH₂)₅-CH₃).

³¹P (D₂O, 300MHz): A single peak appears at 2.0ppm. A sealed melting-point tube containing 90% H₃PO₄ was inserted as internal standard. Two clearly separated peaks appear, indicating two different phosphorus species.

7. Alkylation of Benzene

An acid catalyst was prepared by mixing 1-butyl-3-methylimidazolium-HSO₄ (BMIM HSO₄) salt as prepared in Example 2 above with sulphuric acid with cooling in ice with stirring for 1 hour. The resulting acid catalyst was added to 5 g of benzene and 5.6 g of 1-decene in a glass batch reactor with stirring. Samples of the reaction medium were taken by pipette at intervals of 10 minutes, which were subsequently analysed by Gas Chromatography (CP Sil-5 column) in order to determine the extent of reaction. After 5 hours, stirring was stopped and the catalyst separated from the reaction medium by decantation. To prevent further reaction by any residual catalyst, 1 ml of the reaction medium was then washed by shaking with 5 ml of distilled water for 10 mins.

8. Comparative Example - Alkylation of Benzene

A catalyst not according to the present invention was prepared by addition of sulphuric acid in the same amount as Example 7 to 5 g of benzene and 5.6 g of 1-decene in a glass batch reactor with stirring. Samples of the reaction medium were taken by pipette at intervals of 10 minutes, which were subsequently analysed by Gas Chromatography (CP Sil-5 column) in order to determine the extent of reaction. After 5 hours, stirring was stopped and the catalyst separated from the reaction medium by decantation. To prevent further reaction by any residual catalyst, 1 ml of the reaction medium was then washed by shaking with 5 ml of distilled water for 10 mins.

The table below shows the relative reaction performance of the acid catalysts for alkylation of benzene with 1-decene. Experiment A employed a conventional acid catalyst (sulphuric acid) while Experiments B to D employed the acid catalysts of the present invention.

Table: Acid catalysis of the alkylation of benzene with 1-decene.

Experiment	BMIM HSO ₄ in the catalyst system (mass %)	Reaction time for 40% conversion	Selectivity to monoalkylated product (at 40% Conversion)
A	0	10	63
B	4.8	10	68
C	12.3	100	74
D	19.4	170	87

5

10

15

20

Claims

1. An ionic liquid which is substantially free of Lewis acidity wherein said ionic liquid is obtainable by reacting (a) an organo-nitrogen compound or an organo-phosphorus compound which is substantially free of Lewis acidity with (b) a Brønsted acid, in a mole ratio of (a) to (b) of less than or equal to 1 with the proviso that where
5 the Brønsted acid gives up a single proton the mole ratio of (a) to (b) is less than 1.
2. An ionic liquid as claimed in claim 1 wherein the organo-nitrogen compound is selected from the group consisting of aliphatic amines and heterocyclic amines.
3. An ionic liquid as claimed in claim 1 wherein the organo-nitrogen compound has a cation selected from the group consisting of the formula $[NR^1R^2R^3R^4]^+$ or
10 $[R^1R^2N=CR^3-R^5-R^3C=N^+R^2R^1]$ wherein R^1-R^4 can be the same or different and is selected from H or a hydrocarbyl group with the proviso that at least one of R^1-R^4 is a hydrocarbyl group and R^5 is an alkylene group or a phenylene group.
4. An ionic liquid as claimed in claim 1 wherein the organo-phosphorus compound has a cation selected from the group consisting of the formula $[PR^1R^2R^3R^4]^+$ or
15 $[R^1R^2P=CR^3-R^5-R^3C=P^+R^2R^1]$ wherein R^1-R^4 can be the same or different and is selected from H or a hydrocarbyl group with the proviso that at least one of R^1-R^4 is a hydrocarbyl group and R^5 is an alkylene group or a phenylene group.
5. An ionic liquid as claimed in any one of claims 1-4 wherein the Brønsted acid has an anion selected from the group consisting of BF_4^- , PF_6^- , $RCOO^-$, CF_3COO^- , $HO(O)C-$
20 $C(O)O^-$, $HO(O)C.CH_2-C(OH)(COOH)-CH_2.C(O)O^-$, RNO_3^- , $CF_3SO_3^-$, $H_2PO_4^-$, RPO_3H^- , RSO_3^- , $ROPO_3^-$, $ROSO_3^-$ and HSO_4^- wherein R represents a C1-C30 hydrocarbyl group
6. An ionic liquid as claimed in claim 1 wherein the ionic liquid is selected from the group consisting of 1-butyl-3-methylimidazolium hydrogen sulphate and

triethylammonium hydrogen sulphate.

7. An ionic liquid as claimed in any one of claims 1-6 wherein the mole ratio of the (a) to (b) is in the range from 0.00001 to 1.

8. An ionic liquid as claimed in claim 7 wherein the mole ratio of (a) to (b) is in the
5 range from 0.001 to 0.05.

9. A chemical reaction catalysed by an acid catalyst, characterised in that the acid catalyst is or is dissolved in an ionic liquid as defined in any one of the preceding claims.

10. A chemical reaction according to claim 9 wherein the chemical reaction catalysed by the acid catalyst is selected from the group of reactions consisting of esterification,
10 olefin polymerisation, oligomerisation, alkylation of aromatics, alkylation of isobutane with olefins and the production of caprolactam.

11. Use of an ionic liquid as claimed in any one of claims 1-9 as an acid catalyst or as a solvent for an acid catalyst.

15

20

25

30

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/03150

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 18459 A (BP CHEM INT LTD ;ELLIS BRIAN (GB)) 20 June 1996 (1996-06-20) example 1	
A	EP 0 748 653 A (INST FRANCAIS DU PETROL) 18 December 1996 (1996-12-18) claim 2	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "3" document member of the same patent family

Date of the actual completion of the international search

13 January 2000

Date of mailing of the international search report

31/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Thion, M

INTERNATIONAL SEARCH REPORT

Inter- nal Application No
PCT/GB 99/03150

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 125, no. 19, 4 November 1996 (1996-11-04) Columbus, Ohio, US; abstract no. 246895k, OLIVIER H: "Nonaqueous room-temperature ionic liquids: a new class of solvents for catalytic organic reactions" page 1060; XP002107859 abstract & PROC. ELECTROCHEM. SOC., 1996, -----	
A	FR 2 757 850 A (INST FRANCAIS DU PETROL) 3 July 1998 (1998-07-03) -----	
A	FR 2 626 572 A (INST FRANCAIS DU PETROL) 4 August 1989 (1989-08-04) -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/03150

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9618459	A	20-06-1996	AU 3986495 A	03-07-1996
			CA 2182894 A	20-06-1996
			CN 1140422 A	15-01-1997
			EP 0743878 A	27-11-1996
			FI 963134 A	09-08-1996
			JP 9509888 T	07-10-1997
			NO 963294 A	07-08-1996
EP 0748653	A	18-12-1996	FR 2735399 A	20-12-1996
			JP 9000937 A	07-01-1997
			US 5852130 A	22-12-1998
FR 2757850	A	03-07-1998	US 5892124 A	06-04-1999
FR 2626572	A	04-08-1989	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.